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Hydrocarbon plant—New source of energy for future

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Abstract

The development of alternative sources for energy and chemicals, particularly the use of plant biomass as a renewable source for fuel or chemical feedstocks, has received much recent attention. This paper attempts to review the work carried out by many workers on evaluation of some plant materials as source of energy and chemical feedstocks and the possibilities of producing hydrocarbon and related chemical products, directly or indirectly. Also an exploratory work carried out at Regional Research Laboratory, Jorhat is discussed. Some future directions, which need to be considered to promote development of these petrocrops, are suggested.

Keywords: Hydrocarbon plant; Petrocrops; Bio-crude; Energy

Contents

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1. Introduction

World energy scene is undergoing a period of transition. As the inevitability of exhaustion of fossil fuels is becoming increasingly intensive, efforts are on to find and use substitute form of energy. The large dependence of most societies in the world on petroleum lends importance to hydrocarbon supplies on a self-sustaining and renewable basis. The bio-energy system makes a significant contribution to the world's growing energy needs. The renewable sources would only be able to compete with the fossil fuel resources, if special plant crops containing energy-producing, hydrocarbon-like material are breed and cultivated. The earth has vast areas of land which are unsuitable for food and fodder crops, and recent experience with growing hydrocarbon yielding plants may make it possible to use these large areas for harvesting plants which may yield a substitute for conventional hydrocarbons. Various machines have been developed in the last several decades, which are based on the use of liquid hydrocarbon mixture of appropriate chemical aggregate composition and desirable physico-chemical and performance parameters. There are several compelling reasons for seriously exploring the prospects of hydrocarbon plantations. First, the prospects of increased dependence on oil imports pose a difficult challenge. Secondly, oil prices are likely to go up substantially in the next 10–15 years. Further, it is becoming increasingly evident that woody plants, which are often grown on relatively good soil, will not meet all the demand for fuel wood particularly in countries like India. Petrofarming could, therefore, provide a welcome solution to some of these problems, even though no substantive claims can be made on the viability of this option at present. Various workers have conducted extensive screening program in an attempt to identify potential bio-crude and botanochemical feedstocks.

Before discussing the efforts in developing petroleum plantations and growing green factories for the production of hydrocarbon-like material, it is necessary to describe briefly some of the energy sources available and their constraints, the concept of using plants for material production in the world and finally the creation of a controlled experiment in the growth and harvesting of particular plant for their oil content and hydrocarbon contents. Natural gas, coal and oil (all fossilized photosynthetic products) provide a little more than 95% of the world energy supply; the rest of our resources are very small in comparison. The supply of fossil hydrocarbon would gradually be exhausted, in due course. King Hubbert, a geologist for the US geological survey, was discussing this problem publicly, how fuels, specifically oil and coal, will come into and go out of use [1]. King Hubbert was probably correct in his guesstimates and oil might even peak out before 2050. The methods to increase the energy prospect were those that use sunshine in some useful way, with a minimum environmental problem. Then the idea came in mind that green plants could catch the sun and reduce the carbon, particularly on the equator where plants are the most productive. Through the mechanism of the photosynthetic carbon cycle, the green plant captures the carbon dioxide from the atmosphere and with the aid of sunshine, separates

hydrogen from the water to reduce the carbon dioxide first to carbohydrate in which there is only one oxygen atom on each carbon atom. Eventually, some plants can take the carbohydrate and reduce it all the way to hydrocarbons, with no oxygen at all on the carbon atoms. This is essentially what petroleum is.

2. Screening and processing of biomass for bio-crude

The first efforts to cultivate hydrocarbon-producing plants for fuel production were made by the Italians in Ethiopia (*Euphorbia abyssinica*, 1935–1936) [2] and the French in morocco (*Euphorbia resinifera*, 1940) [3]. Professor Melvin Calvin (Calvin, 1977) revived the idea that hydrocarbon-producing plants could be used as future oil and other chemical sources. He also suggested that the energy farming concept should be given due importance. The plant families mainly Euphorbiaceae and Asclepiadaceae were screened for assessing their suitability as a source of low molecular weight (mw) and non-polar petroleum-like hydrocarbons. Air-dried plant materials were successively extracted with acetone and benzene, and the extracts were analyzed spectroscopically for yield of rubber, wax, glycerides, isoprenoides and other terpenoides. The mixtures of hexane–methanol and heptane–methanol were used for extraction. Yield of 10 barrels of oil/ha/year from each species has been claimed without any genetic improvement. Based on biomass yield of 25 tonn/ha/year, the total energy in the form of liquid fuel from *Euphorbia lathyris* was calculated to be 48 MJ/ha/year, 26 MJ as hydrocarbon and 22 MJ as ethanol. The product of extraction of *E. lathyris* represented a new possibility for a future energy and material source, which was also later on suggested by Nemethy et al. [4–7]. Every *Euphorbia* species contained latex, which was an emulsion of about 30% terpenes in water. The latex hydrocarbon was largely a C_{30} triterpenoid, which could be cracked like oil to make high-octane gasoline. The plant, *E. lathyris* was found to be as a potential ‘gasoline tree’. Some of the latex sterols of *E. lathyris* latex could also be used in pharmaceutical industry and as such could be of more value than the actual crude oil obtained. Another species *Euphorbia tirucalli*, which grows prolifically in various parts of the world, was cultivated for oil, but it required more water for cultivation than *E. lathyris*.

An extensive screening program was conducted by Buchanan et al. [8–13], by taking 200 plant species covering 57 families for their suitability as renewable source of hydrocarbon, protein, carbohydrate and rubber. Each species was rated according to botanical characteristics and potential as multi-use hydrocarbon-producing plants. In the botanical evaluation, plants were rated on a scale of 1–5 with numerical rating of 1 (highest value) assigned to vigorous growing perennial species that could potentially be harvested by clipping with rapid regrowth from rootstock. Thus, species with a cumulative scoring of 11 or less were considered as possibilities for development as a bio-crude producing up to 22.4 tonn/ha/year of dry matter.

An analytical screening program has been conducted by the USDA [14–19] to evaluate and identify plant species as source of high energy, easily extractable compounds suitable for fuel, chemicals and petroleum-sparing chemical feedstock. Plant families that yielded more than one promising species were Anacardiaceae, Asclepiadaceae, Caprifoliaceae, Compositae, Eupforbiaceae and Labiaceae.

Augustus et al. [20,21] screened 22 taxa of Western Ghats of India as potential alternative crops for renewable energy, oil, hydrocarbon and phytochemicals. The highest hydrocarbon yields were observed in *Carissa carandas* (1.7%), and *Jatropha gossypifolia*

(1.7%). The highest polyphenol fraction was observed in *Dodonaea viscosa* (17.1%), *C. carandas* (7.7%), *Swietenia mahagoni* (6.6%) and *Jatropha glandulifera* (6.2%). The highest oil content was observed in *Aganosma cymosa* (10.3%), *C. carandas* (5.8%) and *Argemone mexicana* (5.0%). *S. mahagoni* yielded the highest protein content with 8.1%. The gross heat value of 4175.0 cal/g (17.5 MJ/kg) for *Lochnera rosea*, and 4112.0 cal/g for *Dalbergia sissoo* were the highest among the species analyzed. NMR spectra of the hydrocarbon fractions revealed the presence of *cis*-polyisoprene (natural rubber) and *trans*-polyisoprene (gutta). *Cis*- and *trans*-polyisoprenes are potential alternative energy sources for fuel and/or as industrial raw materials. The potential exists for growing these alternate crops in areas of underutilized lands, subsequently stimulating industrial and economic growth.

Adams [22] and Adams et al. [23–27] also evaluated 80 species using cyclohexane–methanol solvent for extraction for establishing the potential of *Asclepias speciosa* as an energy crop for production of renewable hydrocarbon fuel. The dried plant materials were extracted successively with hexane and methanol affording 3.8 and 17.5% extracts respectively. Chemical analyses of non-polar extractables of the aerial parts of this plant showed that pentacyclic triterpenoids and sterols accounted for 90% of the refined hexane extract. The methanol extract consisted mainly of sugars. The residual plant material appeared to be non-toxic and equivalent to alfalfa hay in digestibility by sheep. Bio-crude content ranged from 4–11% on dry weight basis. Utilization of hexane extractable bio-crude of *A. rotundifolia* as a source of liquid fuel was also explored.

An analytical programme was also conducted by Emon and Seiber [28] on two milkweeds *A. speciosa* and *Asclepias curassavica*. They studied on both the plant materials and latex extracted from the plant and found that these milkweeds were excellent species for their high-calorie contents and organic composition. *A. speciosa* was found to have a greater potential than *A. curassavica* for use as fuel owing to higher calorie content in the latex. The latex of *A. speciosa* was found to contain more reduced chemicals like α and β amyrin, amyrin acetates, and *cis*-polyisoprene, while *A. curassavica* latex contained primarily cardiac glycosides. In fact, *A. speciosa* was found to possess physical and chemical properties comparable to *Euphorbia* spp., which were considered for use as fuel and/or chemical feedstock. *A. curassavica,* due to its higher content of toxic cardiac glycosides and lower energy content, could perhaps be useful for production of specialty chemicals, rather as an energy plant.

During World Wars I and II, there was an avid interest in cultivating various *Asclepias* species as sources of numerous strategically important plant products particularly kapok and rubber [29].

Mclaughlin and Hoffmann [30] also surveyed in south United States and north Mexico and found 195 plants as potential feedstock for bio-crude production. Cyclohexane–ethanol was used for extraction and it was found that *Euphorbia* and *Asclepias* contained high amounts of bio-crude. The bio-crude was also extracted from resinous species of the family Compositae, tribe Astereae.

Roth et al. [31–33] also studied 508 plant species for extraction of bio-crude oil, polyphenols and proteins. Erdman and Erdman (1981) have also studied on evaluation of *Calotropis procera* as a potential source for bio-crude. Dried whole plant material afforded 4.35% of hexane and 16.14% of methanol extracts. Hexane extract was found to be rich in hydrocarbon and the ratio of carbon and hydrogen was similar to that of crude oil and heat value content was comparable to that of crude oil, fuel oil and gasoline.

Carruther et al. [34] also estimated bio-crude potential of this plant in northern Australia. Studies were also carried out on other species for their suitability as a potential sources for hydrocarbon-like materials and chemical feedstocks.

In Romania, Simionescu et al. [35,36] studied on some latex-bearing plants and found that the rough latex extracted with cyclohexane (4–5%) was separated by means of acetone into two fractions, one insoluble in acetone, which contained oils, fatty acids, waxes, terpenes and so on.

Fresh water algae *Botrycoccus braunii* was found to yield liquid hydrocarbons to the extent of about 30% of dried sample. Maxwell et al. [37] reported that this hydrocarbon like material contained up to 70% of $C_{34}H_{58}$ hydrocarbon called botryococcene. These hydrocarbons were either linear compounds C_nH_{2n-2} and C_nH_{2n-4} ($n = 25$, 27, 29 and 31) or branched chain compounds C_nH_{2n-10} ($n = 34$, 36 and 37). The hydrocarbon oils of *B. braunii* could be recovered by solvent extraction and would then need to be cracked, hydrogenated and reformed in order to obtain the conventional transport fuels [38–41].

Pittosporum resiniferum is a tall tree, bearing fruits bigger than a golf ball, the orange pulp of which, when pressed, yielded sticky oil that resembled to petroleum. The oil consists of mainly α pinnene (38%), myrcene (40%), *n*-nonane (3%) and heptane (5%) [6,42].

Margaris and Vokou [43] carried out some experiments in Greece to study the energy-rich plants available in the forests. Among the plant species studied were some Euphorbiaceae, 60 species of euphorbia found in almost all altitudes and existing habitats from marshes to forest.

3. Extraction and characterization of plant extracts

The most detailed study on extraction procedures published till recently was that by Buchanan et al. [8–10] on *Asclepias syriaca*. The plant materials were extracted in a soxhlet apparatus first for 48 h by using a polar solvent (acetone, methanol, etc.) followed by another 48 h extraction with a non-polar solvent such as hexane or cyclohexane. The solvents used for extraction of hydrocarbon fraction were the mixtures of benzene and hexane. In this fractionation procedure, crudely fractionated products were obtained. Oil fractions were examined by thin layer chromatography and hydrocarbon fractions were examined by infrared (IR) spectroscopy to determine whether they were natural rubber, waxes or mixtures. The natural rubber samples were again examined by proton nuclear magnetic resonance (PMR) and gel permeation chromatography (GPC) (Figs. 1–3).

Swanson et al. [44] extracted natural rubber from different plant species by following the above procedure of Buchanan et al. [8–10]. Samples of the dried hydrocarbon fractions were dispersed at room temperature in tetrahydrofuran (THF). The mw and molecular weight distributions (MWDs) were compared by GPC for rubber, guayule and havea.

Twenty-eight taxa of *Helianthus* collected throughout the United States were extracted for oil, polyphenol, hydrocarbon and protein by Seiler et al. [19]. They used acetone for 48 h soxhlet extraction. The acetone was then evaporated using a stream of nitrogen. The air-dried extract was partitioned between hexane and water:ethanol to obtain fractions referred to as oil and polyphenol. The residues were again extracted with hexane for hydrocarbons. Hydrocarbons were examined for the presence of rubber, gutta and waxes. Rubber and gutta were analyzed for weight average mw and MWD. The same procedure

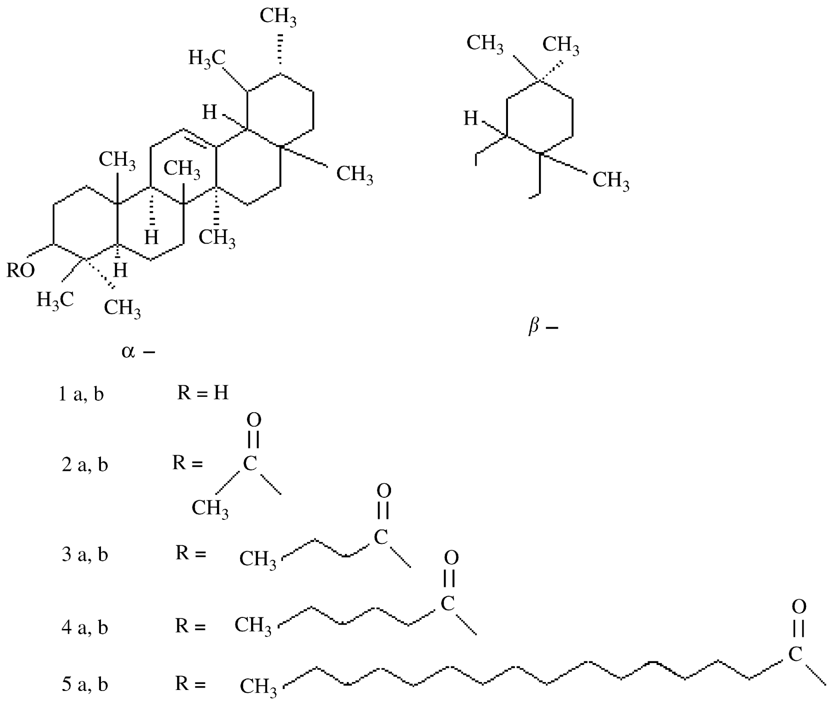


Fig. 1. Structure of the major triterpenols and their esters which occur in *Asclepias speciosa*.

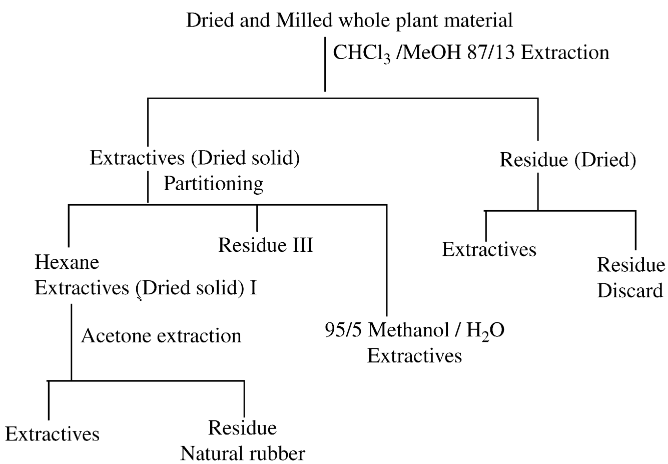


Fig. 2. Separation scheme for *Asclepias linaria* and *Ilex verticillata* extracts.

of extraction was followed by various workers in different parts of the worlds [16–18, 45–49].

Roth et al. [32] evaluated many leguminous plants at Northern Regional Research Center, USDA, USA, by using the soxhlet extraction with acetone first and then with

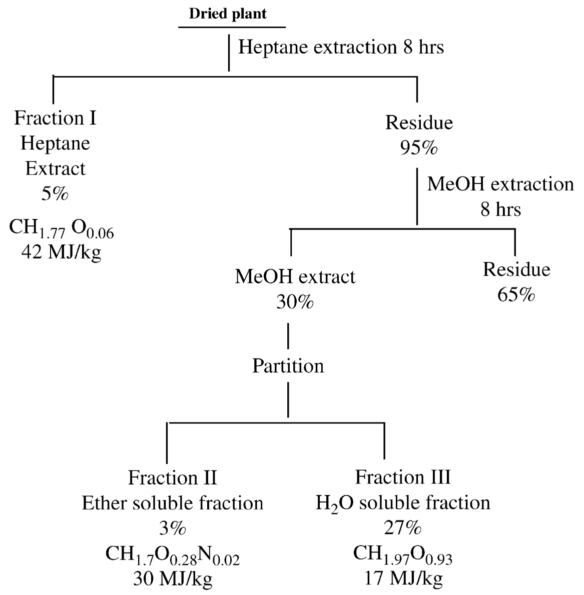


Fig. 3. Scheme of extraction.

cyclohexane from the whole plant excluding roots. The oil fractions were quantitatively analyzed for classes of compound by TLC-flame ionization detection.

The major extractable components of two species *Asclepias linaria* and *Ilex verticillata* were extracted for 24 h in a stainless steel soxhlet extraction apparatus with 87/13 chloroform/methanol by Abbott et al. [14]. The residues were again extracted by water and the extractives were partitioned between hexane and methanol water mixtures. The methanol extracts were again extracted by acetone and the residues were identified as natural rubber. Initial chromatographic separation of the hexane/acetone soluble fraction was accomplished on LC/system 500 chromatograph by sequential elusion with hexane, toluene, dichloromethane and methanol. By IR, HPLC, droplet counter current chromatography and thin layer chromatography, the compounds were identified and confirmed.

Mclaughlin and Hoffmann [30] used another procedure of extraction from which direct estimation of unit cost for production of bio-crude and energy for every species was evaluated. This procedure was also followed previously by Hinmann et al. [50], where the plant materials were extracted with 300 ml of cyclohexane for 12 h followed by a second extraction with 300 ml of ethanol for 12 h using soxhlet apparatus. Energy values for the two extracts and the residues were estimated from elemental analyses of each fraction from several species.

Eardman and Eardman [51] extracted the bio-crude in a soxhlet extractor for 9 h with hexane. Subsequent extractions with methanol from the hexane extract residue were carried out. Gross heat value was determined by bomb calorimetry. Total carbon, hydrogen and oxygen determinations were performed by pyrolysis using Perkin Elmer model 240 analyzer and model RO 17 Leco oxygen analyzer connected to an IR spectrophotometer.

Mcchesney and Adams [52] at University of Mississippi, USA, conducted experiments to evaluate plant species as potential botanochemical source for petroleum substitution compounds as well as for antibacterial, antifungal properties. The extracts were obtained by soxhlet extraction for 22 h with cyclohexane followed by methanol for 22 h. The methanol extracts were concentrated and dissolved in a mixture of ethyl acetate and water.

The plant species *E. lathyris* was extracted in soxhlet apparatus with boiling solvent heptane for 8 h by Nemethy et al. [4]. The residue was then extracted with methanol for 8 h. The extracts were further examined by gas chromatography with high-resolution mass spectroscopy. This procedure for extraction was followed by other scientists like Ayerbe et al. [53] in Spain, Clark et al. [54] in USA and Sharma et al. [55] in India.

Gnecco et al. [56] in Chile carried out an experiment on *Euphorbia* species, where they extracted the bio-crude with CH_2Cl_2 for 30 days at room temperature from chopped fresh plant. The plant was then oven dried, ground and extracted again for 30 days. After removal of solvent, the material obtained was extracted with acetone. Representative fractions were characterized by quantitative analysis, IR spectroscopy, ^{13}C and ^{1}H-NMR spectroscopies and mass spectrometry.

Emon and Seiber [28] collected latex from *A. currassavica* and *A. speciosa* plants. Latex samples were dried under vacuum at 20 °C for at least for 2 days. The latex was refluxed with acetone (60 ml) for 8 h, and then gravity filtration was done. The acetone insoluble residue was refluxed with methanol (40 ml) for another 8 h. The latex extracts were analyzed by NMR, GC, GC-MS and IR spectroscopies.

The latex of *A. syriaca* was extracted with cyclohexane in a soxhlet apparatus for 10 h with 80 °C temperature [35,36]. The extracts were cracked with the help of suitable catalyst and the fractions were analyzed by GC and NMR spectroscopies.

Hammouda et al. [57] in Egypt collected samples of latex by incision of small branches of *Euphorbia* in methanol. The methanol preserved latex was evaporated in vacuum and the residue was exhaustively extracted with $(CH_3)_2CO$. The $(CH_3)_2CO$ extract was dissolved in 600 ml methanol:water and partitioned with *n*-hexane. The hexane extract was dissolved in hot $(CH_3)_2CO$ and left overnight. All the fractions were then characterized by TLC, GLC and mass spectroscopies.

4. Processing of bio-crude for fuels

Mobile oil corporation converted methanol into gasoline, using zsm-5 zeolite as catalyst [58,59], and later the capability of catalytic production of high-grade fuel (gasoline) from biomass compounds like jojoba oil, rubber latex from *Havea brassilensis,* corn and castor oils using similar catalyst was also studied. Biomass compounds from these crops contained mostly paraffinic alcohols, esters, acids or terpenes and their behavior during catalytic conversion by employing zsm-5 catalyst in presence of hydrogen was found to be similar to that of the products obtained from methanol except their molecular dimensions, for conversion into gasoline and petroleum gases.

Vegetable oils have been hydrocracked using bifunctional catalyst at a 300–693 K/ 100–150 atm. The 80% yield of usable fractions of gaseous hydrocarbons, gasoline and diesel was obtained [60].

Adams et al. [25] and Erdman and Erdman (1981) analyzed extractives from *A. speciosa* and *C. procera*, respectively, mainly for elemental compositions and compared the data

obtained with fossil fuel. The C and H analyses of the hexane extracts of both the plants compared closely to that of fossil fuel.

The bio-crude obtained from *E. lathyris* by Calvin et al. [61], after extraction, was subjected to catalytic cracking with special zeolite catalysts developed by mobile oil corporation. The product obtained contained ethylene (10%), propylene (10%), toluene (20%), xylene (15%), C_5–C_{20} non-aromatics (21%), coke (5%), C_1–C_4 alkenes (10%) and fuel oil (10%). All these materials were useful for petrochemical industrial processes [62–64].

Catalytic cracking of solvent extracted bio-crude of *E. tirucalli* was explored in Philippines [65]. The reaction conditions were quite drastic. High temperature and 12–15 psig pressures were employed in a catalyst to feed ratio of 1:1. In one typical run with catalyst at feed ratio of 1:1, temperature 650 F and reaction time 7 h, the resultant products contained non-condensable gases 69.23%, condensable gases (light oil) 21.54% and residue 9.23%. In all their experiments, emphasis was laid on the production of heavy oil [42]. Bio-crude from *E. lathyris* and *Synadenium grantii* were also liquefied using COM catalyst in the presence of hydrogen [66].

A comparison of cracked products obtained from *A. speciosa* (hexane extract), *E. lathyris* (acetone extract) and *Grindelia squarrosa* (methylene chloride extract) was also carried [67]. Fluidized bed cracking of *A. speciosa* gave high yields of light gases (11%) and gasoline (58%) and low yields of diesel and heating oil. Cracking of extracts of *E. lathyris* and *G. squarrosa* by the mobile group using zsm-5 zeolite as catalyst gave good yield of middle distillates. It was observed that better liquid yields with increased middle distillates could be obtained by changing the fluid bed to fix bed reactor. Cracking of *E. lathyris* and *G. squarrosa* resulted in 68% of liquid product comprising of 52% gasoline and 16% of middle distillates. In the case of the fixed bed reactor, the liquid yield was 78%, comprising of 36% gasoline and 42% middle distillates. Cracking of *G. squarrosa* bio-crude in a fixed bed reactor resulted in 74% liquid yield, of which, the yields of gasoline and middle distillate were 14% and 60%, respectively.

Hydrocracking of vegetable oils using a bifunctional catalyst (Al_2O_3-supported RH) yielded 80% of usable fractions of gaseous hydrocarbons, gasoline and diesel [60].

Conversion of bio-crudes, processed from latex of *Euphorbia royleana* and biomass of *C. gigantia* to hydrocarbon fuel, preferably to middle distillate was studied. Craig and Coxworth [68], using a fluidized bed pilot plant reactor and a high-activity zeolite catalyst, evaluated the characters of extracted plant oil from *A. speciosa*. The yields obtained from the FCC pilot were significantly same as that from commercial yields. The gasoline produced from the plant oil had a very high octane number. Analysis of the gasoline showed that the increase in octane number was due to highly aromatic nature of the product.

Simionescu et al. [35,36] studied on catalytic cracking of latex extracted from *A. syriaca*. As a result of the cracking process, the following products were obtained: gases (15–21% in weight), liquids (51–57%) and a solid residue (5–8%). The gases after analyses showed C_1–C_4 saturated and unsaturated hydrocarbons. The liquid fraction analyzed by GC and NMR was composed of products similar to those found in autotype gasoline.

The thermogravimetric studies both for hydrocarbon fraction and polyisoprene rubber showed two decomposition stages. The hydrocarbon fraction showed a smaller weight loss as compared to polyisoprene rubber. At the same time, the activation energy calculated for the thermooxidative degradation of the polyisoprene rubber was 3.4 times greater than the hydrocarbon fraction. The difference lies in the higher hydrocarbon fraction, which was

though small in amount showed that it could not be recommended as a substitute for the polyisoprene rubber. In exchange, the rough latex could be converted to fuel for the diesel engine by cracking process.

5. Work carried out in India

Euphorbiaceae, Asclepiadaceae, Apocynaceae, Urticaceae, Convolvulaceae, Sapotaceae were studied for their suitability as petrocrops by various workers [45,69–75]. Bio-crude potential was determined by preservation and coagulation of latex in case of species amendable to latex tapping. In rest of the species, the dried biomass was extracted with hexane–methanol. Bio-crude potential varied from 26–29%, whereas for other species like *Euphorbia antisyphilitica*, 8.46%. This study resulted in the identification of 17 potential petrocrops.

A new genus *Capaifera* was also evaluated as a source of fuel oil. *Capaifera lingsdorfil* and *Capaifera multijuga* are trees in which a hole is drilled at a height of 90 cm from the ground to tap oil. The wood has a system of canals, which contain oil. It was claimed that this oil could be used directly in an engine without further processing or purification. A single tree yields 20–30 l of oil in 2–3 h in a single tapping and could be tapped twice a year. Capaiba oil, as it is called, consists of 25 different compounds of which each compound is a C_{15} sesquiterpene. Because of its mw and volatility, the material could be used directly in diesel engines [45,69].

Aleurites moluccana was identified as a source of commercially produced lumping oil [76]. The prospects are bright for developing a large industry for processing lumping oil. *Dipterocarpus laevis*, a species of plant that is comparable to Capaiba, is famous all over eastern India on account of its thin liquid balsam commonly called wood oil. The property of Capaiba is similar to that of *D. laevis* oil.

Marimuthu et al. [77] also studied 29 laticiferous taxa of different families for their suitability as alternative sources of renewable energy, rubber and other phytochemicals and selected the most promising ones for large-scale cultivation. They found that the majority of the species under investigation might be considered for large-scale cultivation as an alternative source of rubber, intermediate energy and other chemicals.

Another plant, *Pedilanthus tithymaloides*, was found to be a potential petrocrop with high biomass and hydrocarbon yields [78]. In India, it is cultivated as ornamental or hedge plant or even grown in marginal wastelands. Plant species like *P. tithymaloides* var. cuculatus, *P. tithymaloides* var. verigatus and *P. tithymaloides* (proper) were found to be the promising varieties for development as petrocrop.

Sharma and Babu [48] carried out a preliminary study at Dehradun, India, on five latex-bearing plants. Chlorophyll, terpenes and other polar compounds could be obtained from these plants by extraction with acetone. Subsequent extraction of the plant materials with petroleum ether and benzene yielded hydrocarbon, which could be utilized as liquid fuels. *Gravellea robusta* and *Hakea saligna* contained long chain *n*-alkyle (C_{14}) resorcinol derivatives.

6. The economics of plant hydrocarbon production

There are a few reports available on the economic aspects of production and utilization of hydrocarbon-producing plants in India. This is because we have not reached the stage of

producing hydrocarbon plants on a large scale and the conversion processes have yet to be standardized.

In the United States, Calvin [79–81] began his work with experimental planting of *E. lathyris* and *E. tirucalli*. His preliminary results on the chemical analysis of both whole plant extractions and latex proved that planting produced oil at the rate of 8–12% of the total dry weight. The result of a preliminary economic study of a conceptual process, including biomass operation and a processing plant that extracted the oil material, indicated a cost of $3 to 40 per barrel for the oil extract. According to him the hydrocarbon yield from plant could be improved by proper selection of species and genetic manipulation, just as Malayasia improved the yields of rubber trees.

The Japanese had developed a plantation in Okinawa with great success. They achieved a production of 25–50 barrels of oil per hectare per year. The Japanese expanded their acreage and were making substantial efforts to develop a suitable extraction process for the latex [1,82].

The economics or profitability of producing oil from *P. resiniferum* was also studied. Initial observations in the Philippines showed that a full bearing tree could yield as much 100 kg of fruit per year. Using various oil extraction methods, a hectare of *P. resiniferum* could yield a flammable liquid ranging from 2–28 barrel/ha [83].

Mclaughlin and Hoffmann [30] carried out economic analysis of four potential bio-crude crops. The biomass yields were 7–20 tonn/ha/year and bio-crude yield 126.7 kg/ha/year. The cost of bio-crude per barrel of these species of plant were calculated at $51–154.

Keenan and ASCE [84] discussed the potential for biomass utilization as a source of fuel, petrochemicals and petroleum-sparing substances.

The direct use of photosynthetic materials, for production of hydrogen, fermentation to organic matters and for thermochemical conversions were thought by many workers [85,86]. Biomass offers a feasible renewable energy source, which can make a significant future contribution to the world energy economy. Process economics however prevents the widespread use of such systems. Improvements in bio-conversion efficiencies and reductions in harvesting and handling cost are needed to improve the economic situation.

Little information is available on the cost of production of biomass and latex/ha/year, to calculate the processing cost of bio-crude from biomass/latex and then to carry out technoeconomic feasibility study. However, the processing cost of 1 kg of bio-crude from biomass and latex processing to liquid fuels worked out to be Rs. 24.6 and 24.2, respectively, for a plant capacity of 25 tonn/year. A continuous-type reactor was the requirement for a plant capacity higher than 25 tonn/year [71].

The idea of using plants to create hydrocarbon-like materials as a substitute for our current fuel and materials sources has become more important, especially in some of the less developed areas of world which have a great deal of land not suitable for food production. Various efforts are being made toward this end in Japan, Thailand, Australia and Spain, and attempts are under way to improve agronomic yields, develop small-scale extraction plants, learn more about the composition of the plant and study possible ways of modifying the biosynthetic routes to produce more desirable end products [1,82]. Therefore, what is needed now is an effort on the part of the agricultural and energy community to commit itself to an energy agriculture, which would have long-term benefits for the entire world.

7. Work carried out in RRL, Jorhat

In Regional Research Laboratory, Jorhat, experiments were carried out to evaluate the chemical compositions of some species of latex-bearing plants available in abundance in the forest of north eastern India. The plant resources in the forest of north eastern India are the richest and largest treasure house of biodiversity. According to a survey, out of the total 5725 endemic species in India, the region has a total of about 1808 endemic species (Nayar, 1996). There are 1500 species of trees, 337 species of climbers and climbing shrubs, 700 species of herbs, 300 species of ferns, 800 species of monocots and 350 species of grasses in the forest of this region [87]. There are 99 species of laticiferous plants, belonging to 63 genera and 25 families that occur in plains and hilly areas of this region and their phytogeographical status, nature of growth, frequency of occurrence and different parts used for various purposes differ from species to species [88]. Therefore, careful preliminary chemical investigations of a few abundantly available latex-bearing plant species were carried out in the first phase. As preliminary investigation 10 species of plants were selected and analyzed for their cellulose content, ash, lignin and CHN content (Table 1). The plant materials were further extracted for crude protein, oil, polyphenol, hydrocarbon,

Table 1
Chemical composition of different species of latex-bearing plants

Species	C (%)	H (%)	N (%)	α cellulose %	Lignin (%)	Ash (%)
Plumeria alba	44.89	6.72	1.26	59.56	26.42	3.76
Calotropis procera	43.49	6.65	1.01	56.42	24.43	5.62
Ficus carica	44.30	6.18	0.98	60.21	27.35	2.18
Erythrina variegata	41.21	6.01	3.83	51.72	21.64	3.41
Euphorbia nerrifolia	40.21	6.01	2.03	57.35	22.67	4.76
Allamanda catherlica	41.28	6.02	2.93	55.42	23.87	6.23
Nerium indicum	38.19	5.97	1.63	53.64	26.41	2.34
Tabernaemontana divarieta	37.81	5.83	2.03	61.24	25.51	4.56
Mimusops elengi	44.28	6.21	2.34	51.46	29.65	5.18
Euphorbia pulcherima	42.26	6.00	1.64	53.73	25.64	3.42

Table 2
Analytical data of different species of latex-bearing plants

Species	Oil (%)	Polyphenol (%)	Hydrocarbon (%)	Unsaponifiable (%)	Fat (%)	Protein (%)
Plumeria alba	3.56	7.89	1.36	49.3	26.8	7.87
Calotropis procera	3.07	8.42	2.04	64.3	24.3	11.26
Ficus carica	1.21	4.26	0.94	68.4	21.2	8.21
Erythrina variegata	1.01	5.26	0.29	58.9	27.4	7.62
Euphorbia nerrifolia	3.87	12.49	3.28	56.4	30.6	12.68
Allamanda catherlica	1.38	7.24	1.26	46.2	21.8	8.16
Nerium indicum	3.01	8.25	1.48	51.2	24.4	10.21
Tabernaemontana divarieta	1.36	7.42	0.86	62.1	31.5	9.26
Mimusops elengi	5.37	10.26	3.12	52.6	24.7	11.23
Euphorbia pulcherima	3.94	8.42	2.41	55.7	28.3	9.42

Table 3
Chemical constituents of the plant biomass

Species	Family	Plant parts	Harvest moisture content (%)	Oil (%)	Polyphenol (%)	Hydrocarbon (%)
Plumeria alba	Apocynaceae	Leaf	87.5	0.21	3.86	0.26
		Stem	56.8	3.36	6.84	1.28
		Bark	89.3	4.74	7.62	1.78
		Whole plant	76.3	3.56	6.89	1.36
Calotropis procera	Asclepiadaceae	Leaf	69.1	1.68	2.58	1.06
		Stem	64.6	3.64	3.56	2.47
		Bark	76.9	3.89	3.96	2.60
		Whole plant	71.5	3.11	3.42	2.35
Euphorbia nerrifolia	Euphorbiaceae	Leaf	73.8	2.46	4.67	0.42
		Stem	62.4	3.56	9.63	2.58
		Bark	86.9	4.95	12.68	2.93
		Whole plant	78.6	3.87	11.49	2.28
Nerium indicum	Apocynaceae	Leaf	64.3	2.10	4.21	0.34
		Stem	62.4	3.71	6.23	1.36
		Bark	70.9	3.24	8.25	1.78
		Whole plant	67.2	3.24	7.54	1.45
Mimusops elengi	Sapotaceae	Leaf	65.2	1.36	1.46	1.21
		Stem	57.0	6.54	8.43	3.56
		Bark	61.4	8.21	8.91	3.92
		Whole plant	59.3	6.87	7.69	2.42

unsaponifiables and free fatty acid by using various solvents (Table 2). By adopting standard procedure and after generating analytical data, five of these species were finally selected for the study.

The quantitative amounts of different compounds like hydrocarbon, oil, polyphenol, etc. in different parts of the plants as well as whole plant were determined (Table 3). The chemical constituents of the oil fractions extracted from the plant species were saponified and characterized for identification of compounds. They are mostly sterols, fatty acids, triglycerides, non-glyceride waxes. Hydrocarbon fractions were characterized with the help of IR, ^{1}H-NMR, ^{13}C-NMR, GC-MS and thermal analyses. The compounds were identified as polyisoprene type of rubber and other hydrocarbon-like compounds. The gross heat value and CHN of the hydrocarbon fraction were found to be comparable with that of crude oil, gasoline, lignite coal (Table 4). By studying their physico-chemical characteristics, biomass production; the plant species will be suggested for large-scale cultivation as an alternative source for producing hydrocarbon and chemical feedstocks.

8. Conclusion

It is clear from the discussion that an increase in our dependence on petroleum products as projected will impose unusually heavy burdens on the economic development in the

Table 4
Characteristics of plant biomass, extractives and fossil fuels

Species		Carbon (%)	Hydrogen (%)	Nitrogen (%)	Ash (%)	Gross heat (cal/g)
Plumeria alba	Plant biomass	44.89	6.72	1.26	3.76	5426
	Hexane extract	76.98	8.05	0.49	0.50	8325
Calotropis procera	Plant biomass	43.49	6.65	1.01	5.62	6145
	Hexane extract	74.13	11.34	0.37	0.65	9837
Euphorbia nerrifolia	Plant biomass	40.21	6.01	2.03	4.76	5132
	Hexane extract	76.30	10.88	0.30	0.82	9218
Nerium indicum	Plant biomass	38.19	5.97	1.63	2.34	4405
	Hexane extract	72.46	11.12	0.34	0.74	7145
Mimusops elengi	Plant biomass	44.28	6.21	2.34	5.18	4590
	Hexane extract	78.67	12.35	0.28	0.45	8924
Anthracite coal[a]		79.70	2.90	—	9.60	7156
Lignite coal[a]		40.60	6.90	—	5.90	3889
Crude oil[b]		84.00	12.70	—	—	10506
Gasoline[b]		84.90	14.76	—	—	11528

[a][89].
[b][90].

future. While every effort has to be made to conserve and to utilize petroleum efficiency in the Indian economy, it is essential to launch a major effort in exploring and developing substitute supplies of hydrocarbons. Some of the plants discussed here present interesting possibilities for the future, but their viability and production on a large-scale would be dependent on the success achieved by us in research and development in this field over the next few years. The importance of sustained and large-scale research and development activity in this field requires the articulation of a well-conceived and clear strategy. Therefore, extensive research is needed on screening and selection of plant species that are more suitable for specific sites, soil and climatic conditions prevalent in the different parts of the country. As most of the species are wild, agro-technology for cultivation of these species needed to be standardized. Efforts may be needed to increase the bio-crude potential of these species through genetic manipulation. Also, emphasis is to be given on developing the quality of the bio-crude and suitable catalyst for the reaction to get fuels of desirable quality. Therefore, approach for maximizing biomass productivity and increasing bio-crude content with quality product should be adopted which will help to alleviate the scarcity of petroleum products as well as create healthy environment.

The following areas of biomass resource-based energy programme are specifically suggested for detailed investigation:

(I) Adoption of massive afforestation energy plantation projects in the areas not used for conventional agriculture.
(II) Conversion of non-edible oils to diesel substitutes and large-scale trials of such a possibility.
(III) Bio-conversion of ligno-cellulosic biomass to ethanol in an integrated system incorporating the production of bio-gas, bio-fertilizer and sugar for industrial applications.
(IV) Large-scale and organized production of aquatic biomass species like algae, water hyacinth, etc. for integrated development of an energy–food–ecology system.
(V) Thermochemical and chemical conversion of biomass in small- and large-scale sectors to production of gaseous and liquid fuels and chemical feedstocks.

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